Indicator: Nitrate and Pesticides in Groundwater in Agricultural Watersheds (033)

Nitrogen is a critical plant nutrient, and most nitrogen is used and reused by plants within an ecosystem (Vitousek, et al., 2002). Thus, in undisturbed ecosystems, minimal "leakage" occurs into either surface runoff or ground water, and concentrations are very low. However, when nitrogen fertilizers are applied in amounts greater than can be incorporated into crops or lost to the atmosphere through volatilization or denitrification, nitrate concentrations in groundwater can increase. Elevated nitrogen levels also might come from disposal of animal waste, onsite septic systems, sewage treatment plants, or in the form of atmospheric deposition. Nitrate contamination in shallow ground water (less than 100 feet below land surface) raises potential concerns for human health in infants, particularly in rural agricultural areas where shallow ground water is used for domestic water supply. Concentrations above the federal drinking water standard of 10 mg/L may pose a risk of methemoglobinemia or "blue baby syndrome," a condition that interferes with oxygen transport in the blood of infants (EPA, 2004).

More than one billion pounds of pesticides are used in the U.S. each year to control weeds, insects, and other organisms that threaten or undermine human activities (Aspelin, 2003). About 80% of the total is used for agricultural purposes. Although pesticide use has resulted in increased crop production and other benefits, pesticide contamination of groundwater poses risks to human health if contaminated groundwater is used as a drinking water source – especially if untreated.

This indicator is based on groundwater samples collected between 1992 and 1998 as part of the U.S. Geological Survey's National Water Quality Assessment (NAWQA) Program. During this period, NAWQA analyzed stream and groundwater samples from 36 major river basins across the conterminous United States. Groundwater samples were collected from existing wells where possible, and for consistency, all samples were targeted at the uppermost layer of the aquifer. Most wells were sampled once; a few were sampled multiple times as part of a detailed nutrient study, and the results averaged. This indicator reports concentrations of nitrate and pesticides in groundwater samples collected in predominantly agricultural watersheds. A related indicator reports concentrations of nitrate and pesticides in streams that drain agricultural watersheds (Indicator "Nitrate and Pesticides in Streams in Agricultural Watersheds").

The nitrate component of this indicator covers 1,190 wells in agricultural watersheds, with concentrations reported in mg/L. Results are compared with the federal drinking water standard of 10 mg/L, which is EPA's Maximum Contaminant Level (MCL).(U.S. EPA, 2005). MCLs are enforceable standards representing the highest level of a contaminant that is allowed in drinking water. MCLs take into account cost and best available treatment technology, but are set as close as possible to the level of the contaminant below which there is no known or expected risk to health, allowing for a margin of safety.

Pesticide data come from a subset of 1,068 wells that NAWQA screened for a list of 73 pesticides and 7 selected pesticide degradation products. This suite of chemicals accounts for approximately 75% of the total amount of agricultural pesticides applied annually in the United States by weight (USGS, 1999). Three types of U.S. EPA human health-related standards and guidelines were used to evaluate pesticide data: Maximum Contaminant Level (MCL) (as described above), Risk-Specific Dose (RSD), and Lifetime Health Advisory (HA-L) (U.S. EPA 2000, 2001). In all three cases, the standard and guideline levels are concentrations pertaining to lifetime exposure through drinking water. The RSD is a guideline for potential carcinogens associated with a specified cancer risk of 1 in 100,000, based on drinking-water exposure over a 70-year lifetime. The HA-L is an advisory guideline for drinking-water exposure over a 70-year lifetime, considering non-carcinogenic adverse health effects. More detail on these types of benchmarks, their derivation, and their underlying assumptions is provided in Nowell and Resek (1994). For this indicator, if a chemical had multiple benchmarks, the MCL took precedence; if no MCL was available, the lower of the RSD (at 1 in 100,000 cancer risk) and HA-L values was selected. An

exceedance was identified if a yearly, time-weighted mean concentration exceeded the relevant standard or guideline (Heinz Center, 2002).

What the Data Show

NAWQA data compiled for The Heinz Center (2002) indicate that on average during the 1992-1998 period:

- Nitrate concentrations were above 2 mg/L in 55% of wells sampled in areas where agriculture is the primary land use (Figure 033-1).
- About 20% of the wells had nitrate concentrations that exceeded the federal drinking water standard (10 mg/L). Concentrations above this range may pose a health risk to infants, as noted above (EPA, 2004).
- Less than 1% of the wells in agricultural watersheds had one or more pesticides in concentrations that exceeded human health standards or guidelines (Heinz Center, 2002). However, as shown in Figure 033-2, about 60% of wells in agricultural areas had a least one detectable pesticide, and 10.6% had an average of five or more compounds at detectable levels.
- A relatively small number of these chemicals, specifically the herbicides atrazine (and its
 breakdown product desethylatrazine), metolachlor, cyanazine, and alachlor, accounted for
 most detections in ground water. The high detection frequency for these pesticides is related
 to their use. All are among the top five herbicides used in agriculture across the nation
 (Kolpin, et al., 1998).

Indicator Limitations

- These data only represent conditions in the 36 major river basins and aquifers sampled by the NAWQA program between 1992 and 1998. While they were subjectively chosen to be representative of watersheds across the United States, they are the result of a targeted sample design. The data also are highly aggregated and should only be interpreted as an indication of national patterns.
- Drinking water standards or guidelines do not exist for 44% (35 of 80) of the pesticides and
 pesticide degradation products analyzed. Current standards and guidelines also do not
 account for mixtures of pesticide chemicals and seasonal pulses of high concentrations.
 Possible pesticide effects on reproductive, nervous, and immune systems, as well as on
 chemically sensitive individuals, are not yet well understood.
- This indicator does not provide information on the extent to which pesticide concentrations exceed or fall below standards, nor the extent to which they exceed or fall below other reference points (e.g., Maximum Contaminant Level Goals (MCLGs) for drinking water).

Data Sources

The data sources for this indicator were the U.S. Geological Survey's National Water Quality Assessment (NAWQA) Program, as compiled for The Heinz Center (2002), http://www.heinzctr.org/ecosystems/farm/pest_strms.shtml. Additional information about the NAWQA

data used in the Heinz Center report can be found at: http://water.usgs.gov/nawqa/heinz_ctr/.

References

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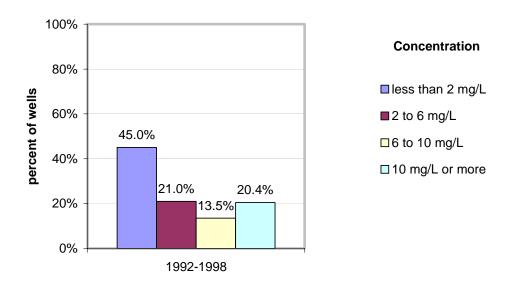
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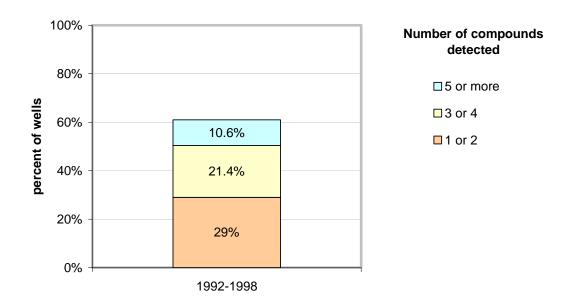
Graphics

Figure 033-1. Nitrate in groundwater in agricultural watersheds, 1992-1998



EPA's drinking water standard is 10 mg/L (Maximum Contaminant Level, or MCL).

Figure 033-2. Pesticides in groundwater in agricultural watersheds, 1992-1998



R.O.E. Indicator QA/QC

Data Set Name: NITRATE AND PESTICIDES IN GROUNDWATER IN AGRICULTURAL

WATERSHEDS

Indicator Number: 033 (89148)

Data Set Source: U.S. Geologic Survey

Data Collection Date: Irregular: 1993-1998

Data Collection Frequency: 1-2yr.

Data Set Description: Nitrate and Pesticides in Groundwater in Agricultural Watersheds

Primary ROE Question: What are the trends in extent and condition of groundwater in the United

States?

Question/Response

T1Q1 Are the physical, chemical, or biological measurements upon which this indicator is based widely accepted as scientifically and technically valid?

This indicator is based on data collected by USGS NAWQA program. NAWQA s overall sample design represents a comprehensive effort to assess the nation s water quality through study units across the lower 48 states, which were chosen to be broadly representative of various land uses and hydrogeologic settings. Gilliom et al. (1995) provides an official description of sample design (full citation in T3Q3). Although aquifer selection was not random, well location was. Data for

this indicator were deliberately collected at or near the top of the water table only (i.e., shallow wells). However, this limitation is appropriate because it ensures that the sample is representative of the groundwater most likely to be consumed by humans, as the purpose of this indicator is to evaluate potential risks to human health. The data for this indicator were collected between 1992 and 1998, a period that covers two full NAWQA sampling cycles and a total of 36 NAWQA study units. Within these 36 study units were several watersheds in which agriculture was considered a significant land use, according to a standard set of criteria described in Gilliom and Thelin (1997) (full citation in T3Q3). Samples from 1,190 wells in these agricultural watersheds were analyzed for both nitrate and pesticides. Although samples were generally only collected once per well, this is considered a scientifically valid way to assess groundwater conditions because changes in groundwater chemistry occur on a relatively slow timescale.

T1Q2 Is the sampling design and/or monitoring plan used to collect the data over time and space based on sound scientific principles?

This indicator is based on data collected by USGS's NAWQA program. NAWQA s overall sample design represents a comprehensive effort to assess the nation's water quality through study units across the lower 48 states, which were chosen to be broadly representative of various land uses and hydrogeologic settings. Gilliom et al. (1995) provides an official description of sample design (full citation in T3Q3). Although aquifer selection was not random, well location was. Data for this indicator were deliberately collected at or near the top of the water table only (i.e., shallow wells). However, this limitation is appropriate because it ensures that the sample is representative of the groundwater most likely to be consumed by humans, as the purpose of this indicator is to evaluate potential risks to human health. The data for this indicator were collected between 1992 and 1998, a period that covers two full NAWQA sampling cycles and a total of 36 NAWQA study units. Within these 36 study units were several watersheds in which agriculture was considered a significant land use, according to a standard set of criteria described in Gilliom and Thelin (1997) (full citation in T3Q3). Samples from 1,190 wells in these agricultural watersheds were analyzed for both nitrate and pesticides. Although samples were generally only collected once per well, this is considered a scientifically valid way to assess groundwater conditions because changes in groundwater chemistry occur on a relatively slow timescale.

T1Q3 Is the conceptual model used to transform these measurements into an indicator widely accepted as a scientifically sound representation of the phenomenon it indicates?

This indicator did not require a great deal of data manipulation. For its report to the Heinz Center, NAWQA simply aggregated the data, reporting average chemical concentrations for groups of wells and summarizing results by land use type. Results are expressed in terms of whether health criteria are exceeded. The health standards and guidelines used in compiling this indicator are documented in T2Q3; all are values that have been scientifically established by EPA.

T2Q1 To what extent is the indicator sampling design and monitoring plan appropriate for answering the relevant question in the ROE?

Overall, the spatial, temporal, and chemical coverage of this indicator are all appropriate for answering the question "What are the trends in extent and condition of groundwater?" in agricultural areas where nitrate and pesticides may be a particular problem. This indicator uses a limited number of aquifers as a basis for generating an overall national indicator. However, the NAWQA program was specifically designed with this in mind, as the program intentionally targeted a sample that was representative of the variety of land-use types and hydrogeologic conditions (e.g., geology, recharge vs. discharge zones, etc.) across the lower 48 states. NAWQA

is currently working on a design to better relate individual well water samples to regional patterns of contamination, but these data are not currently available. Thus, the choice of study aquifers was not random; aquifers were specifically targeted to give a national cross-section. However, well locations within each aquifer were random. NAWQA did not consider data from springs, drains, wells that were too close to other wells, or other locations that might taint or bias the overall result (http://water.usgs.gov/nawqa/nutrients/datasets/nutconc2000/). Beginning in 1991, NAWQA set out to examine 51 study areas, which are shown in the map on NAWQA s website (http://water.usgs.gov/nawqa/). The subsequent 9-year period was divided into three-year cycles, with approximately one-third of the study units sampled intensely during each cycle. This indicator reports data from agricultural watersheds within the 36 study units that were visited during the first two cycles, between 1992 and 1998. The indicator includes data from 1,190 wells that were screened for nitrate and 1,068 that were screened for pesticides. In all cases, samples were taken from the uppermost portions of the aquifer. Thus, results are not indicative of the condition of U.S. aquifers as a whole, but they are indicative of the condition of the groundwater that is most likely to be consumed as drinking water (i.e., pumped from shallow wells). Because this indicator is designed to assess risks from long-term exposure to contaminants in drinking water, NAWQA compared measured concentrations with the most up-to-date and relevant drinking water standards and guidelines available, all of which are based on risks from prolonged exposure. Most wells were only sampled once. However, in a few cases, multiple samples were analyzed, with contaminant concentrations averaged together into a single figure for this report (Bill Wilber, USGS, personal communication, 2005). Because conditions in groundwater are relatively stable (slow flow, slow dispersion), there should be little change in contaminant concentrations on a day-to-day or year-to-year timescale. Thus, even one or two samples should be sufficient for comparison with guidelines for prolonged exposure (Bill Wilber, USGS, personal communication, 2005). In terms of chemicals, this indicator covers a broad range of compounds that may be present as a result of agricultural applications. Nitrate, though it occurs naturally, may also be found in elevated levels due to the presence of runoff from fertilizer as well as human and animal waste. The 73 pesticides and 7 pesticide degradation products screened for this indicator account for approximately 75% of the total agricultural pesticide application in the U.S. by weight (NAWQA: http://ca.water.usgs.gov/pnsp/anstrat/). All are chemicals whose presence may be of concern to humans who use groundwater as their domestic water supply, particularly if it is untreated.

T2Q2 To what extent does the sampling design represent sensitive populations or ecosystems?

This indicator is designed to report the condition of the uppermost portion of aquifers in agricultural regions, as the sample is intended to be representative of the groundwater most commonly used as a water supply for humans, but there was no attempt to target well water sampling at sensitive populations such as infants (nitrate) or people who are particularly susceptible to pesticide contamination.

T2Q3 Are there established reference points, thresholds or ranges of values for this indicator that unambiguously reflect the state of the environment?

EPA has established drinking water standards or guidelines for many of the chemicals screened. The current drinking water standard for nitrate is 10 mg/L, which is EPA s Maximum Contaminant Level (MCL). Pesticide reference thresholds for this indicator are listed at http://oregon.usgs.gov/sumrpt/Benchmrk.1.html and http://oregon.usgs.gov/sumrpt/Benchmrk.2.html, along with the sources of these values. For some pesticide-related contaminants, reference values have not yet been established.

T3Q1 What documentation clearly and completely describes the underlying sampling and analytical procedures used?

All NAWQA groundwater sampling procedures are documented in official USGS reports (full citations appear below). Lapham et al. (1995) documents official procedures for establishing well sites. Because of the expense of drilling, NAWQA sought to sample from existing wells where possible (Bill Wilber, USGS, personal communication, 2005). Koterba et al. (1995) discusses sample collection and preservation, while Koterba (1998) describes procedures for obtaining ancillary data at each well site, including information about the location of the well screen relative to the water table. Laboratory methods are fully documented by USGS. NAWQA measured nitrate concentrations using procedures described in Fishman (1993). Pesticide concentrations were measured using two primary methods: gas chromatography/mass spectrometry (GC/MS) (Zaugg et al., 1995) and high-performance liquid chromatography (HPLC) (Werner et al., 1996). The list of pesticides and degradation products measured is the same as the list used in NAWQA s 1994 summary reports, which included 73 pesticides and 7 related degradation products (list available in two parts, located at http://or.water.usgs.gov/sumrpt/Constits.1.html and http://or.water.usgs.gov/sumrpt/Constits.2.html) (Lisa Nowell, USGS, personal communication, 2005). The website http://ca.water.usgs.gov/pnsp/anstrat/ provides a list of the specific laboratory methods used for each of these chemicals (see Table 2 on this website). Detection limits, which are compound-specific, are listed at the same website. Fishman, M.J. 1993. Methods of analysis by the U.S. Geological Survey National Water-Quality Laboratory--Determination of inorganic and organic constituents in water and fluvial sediments. U.S. Geological Survey Open-File Report 93-125. Koterba, M.T., F.D. Wilde, and W.W. Lapham, 1995, Ground water datacollection protocols and procedures for the National Water-Quality Assessment Program: Collection and documentation of water-quality samples and related data; U.S. Geological Survey Open-File Report 95-399. Koterba, M.T., 1998, Ground water data-collection protocols and procedures for the National Water-Quality Assessment Program: Collection, documentation, and compilation of required site, well, subsurface, and landscape data for wells. U.S. Geological Survey Water-Resources Investigations Report 98-4107. Lapham, W. W., F.D. Wilde, and M.T. Koterba, 1995, Ground water data collection protocols and procedures for the National Water-Quality Assessment Program: Selection, installation, and documentation of wells and collection of related data. U.S. Geological Survey Open-File Report 95-398. Werner, S.L., Burkhardt, M.R., and DeRusseau, S.N., 1996, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory: Determination of pesticides in water by Carbopak-B solid-phase extraction and high-performance liquid chromatography: U.S. Geological Survey Open-File Report 96-216, Denver, Colorado, 42 pp. Zaugg, S.D., Sandstrom, M.W., Smith, S.G., and Fehlberg, K.M., 1995, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory-Determination of pesticides in water by C-18 solid-phase extraction and capillary-column gas chromatography/mass spectrometry with selected-ion monitoring: U.S. Geological Survey Open-File Report 95-181, Denver, Colorado, 49 pp.

T3Q2 Is the complete data set accessible, including metadata, data-dictionaries and embedded definitions or are there confidentiality issues that may limit accessibility to the complete data set?

Water quality data collected by NAWQA may be accessed through the NAWQA database, http://infotrek.er.usgs.gov/servlet/page? pageid=543& dad=portal30& schema=PORTAL30. These data may also be accessible through USGS s general water quality database, located at http://waterdata.usgs.gov/nwis/qw. EPA obtained the data for this indicator directly from the Heinz Center s 2002 report, the State of the Nation s Ecosystems. This report was based on a subset of data that the Heinz Center obtained from NAWQA, which contained a summary of data

from the 1992-1998 NAWQA cycle, with sites and results classified by land-use type. For nitrate concentrations, the report NAWQA prepared for the Heinz Center may be accessed online at http://water.usgs.gov/nawqa/nutrients/datasets/nutconc2000/, although this report lists values for aggregations of wells, not individual wells. This indicator reports data for nitrate plus nitrite, which is often abbreviated as nitrate because concentrations of nitrite are typically small relative to concentrations of nitrate. For pesticide concentrations, the report NAWQA prepared for the Heinz Center does not appear to be available online. However, the Heinz Center does provide access to all data that appear directly in the graphics in its 2002 report, through the following links: http://www.heinzctr.org/ecosystems/farm/datasets/pesticide_significance.shtml.

http://www.heinzctr.org/ecosystems/farm/datasets/pesticide_occurrence.shtml.

http://www.heinzctr.org/ecosystems/farm/datasets/pesticide_occurrence.shtml.

T3Q3 Are the descriptions of the study or survey design clear, complete and sufficient to enable the study or survey to be reproduced?

Reproducibility is inherently limited because this indicator reports historical data. Nonetheless, NAWQA and the Heinz Center have provided several references to document the design of the survey upon which this indicator is based. Gilliom et al. (1995) discusses the overall design of the NAWQA program, while Gilliom and Thelin (1997) provide a good description of how study units were classified as to land use. Scott (1989) describes the organization of land use data into a computer database. NAWQA s report to the Heinz Center (http://water.usgs.gov/nawqa/nutrients/datasets/nutconc2000/sw_nuts_Heinz.xls) includes a list of groups of wells where nutrient (e.g., nitrate) samples were collected for agricultural watersheds, but does not identify specific well sites. However, all raw data for this indicator could conceivably be acquired from the NAWOA database and then queried following the criteria outlined in the sources above in order to replicate the dataset for the indicator. NAWQA has published a full list of the 73 pesticides and 7 related degradation products that were screened for this indicator, which can be found in two parts at http://or.water.usgs.gov/sumrpt/Constits.1.html and http://or.water.usgs.gov/sumrpt/Constits.2.html. This is the same set of chemicals that was discussed in NAWQA's 1994 report (Lisa Nowell, USGS, personal communication, 2005). Aquatic and human health standards and guidelines for this indicator are documented at http://oregon.usgs.gov/sumrpt/Benchmrk.1.html and http://oregon.usgs.gov/sumrpt/Benchmrk.2.html. Gilliom, R.J., W.M. Alley, and M.E. Gurtz. 1995. Design of the National Water-Quality Assessment Program: Occurrence and distribution of water-quality conditions. U.S. Geological Survey Circular 1112. Gilliom, R. J., and G.P. Thelin, 1997, Classification and mapping of agricultural land for National Water-Quality Assessment. U.S. Geological Survey Circular 1131. Scott, J.C. 1989. A computerized data-base system for land-use and land-cover data collected at ground-water sampling sites in the pilot National Water-Quality Assessment Program. U.S. Geological Survey Water-Resources Investigations Report 89-4172.

T3Q4 To what extent are the procedures for quality assurance and quality control of the data documented and accessible?

NAWQA provides several references that describe QA/QC procedures for the collection and analysis of groundwater samples. Martin (1999) provides particularly good coverage of field and laboratory protocols such as field blanks and replicates. NAWQA also discusses how and why certain wells were excluded from this particular analysis (http://water.usgs.gov/nawqa/nutrients/datasets/nutconc2000/). Martin, J.D. 1999. Quality of pesticide data for environmental water samples collected for the National Water-Quality Assessment Program, 1992-96, and examples of the use of quality-control information in water-

quality assessments. U.S. Geological Survey. Accessed January 10, 2003 at http://ca.water.usgs.gov/pnsp/rep/qcsummary.

T4Q1 Have appropriate statistical methods been used to generalize or portray data beyond the time or spatial locations where measurements were made (e.g., statistical survey inference, no generalization is possible)?

This indicator does not require temporal manipulation. Levels of contaminants in groundwater do not generally show much variability on a day-to-day or year-to-year timescale, so a single set of measurements should be sufficient to describe current conditions. In the few cases where multiple samples were collected from the same well, NAWQA simply averaged the results (Bill Wilber, USGS, personal communication, 2005). Spatially, the sample design was designed to provide a broad national picture, so no further extrapolation or generalization is necessary.

T4Q2 Are uncertainty measurements or estimates available for the indicator and/or the underlying data set?

Uncertainty estimates are not available for the exact subset of data included in this indicator. However, NAWQA has published uncertainty figures for the overall data collection effort, which should be indicative of uncertainty for this indicator. Mueller (1998) specifically discusses nutrient (nitrate) data, while Martin (2002) evaluates uncertainty for pesticide data. Mueller, D.K., 1998, Quality of nutrient data from streams and ground water sampled during 1993-95-National Water-Quality Assessment Program, U.S. Geological Survey Open File Report 98-276. Martin, J.D., 2002, Variability of pesticide detections and concentrations in field replicate water samples collected for the National Water-Quality Assessment Program 1992-97, U.S. Geological Survey Water Resources Investigation Report 01-4178.

T4Q3 Do the uncertainty and variability impact the conclusions that can be inferred from the data and the utility of the indicator?

Because uncertainty varies depending on the chemical and analytical method in question, it is difficult to make a single definitive statement about the impact of uncertainty on this indicator. However, because results from over 1,000 wells are generalized over the entire nation, the summary figures reported by this indicator should be considered reasonably accurate. Because this indicator generally relies on samples that were only collected once per well, it does not account for day-to-day or year-to-year variability in groundwater concentrations of the chemicals in question. However, groundwater conditions are assumed to be relatively constant over time; movement of water and dispersion of contaminants are slow processes, particularly as compared with changes in aboveground streams (Indicator 040). Thus, groundwater conditions do not require the same frequency of sampling as conditions in surface water (which NAWQA measured 15-25 times over the course of a given year) to be reflective of long-term trends.

T4Q4 Are there limitations, or gaps in the data that may mislead a user about fundamental trends in the indicator over space or time period for which data are available?

Limitations to this indicator include the following: 1. Data for this indicator only represent conditions in 36 NAWQA study areas, each of which typically encompasses a single major river basin or aquifer. While study units were subjectively chosen to be representative of watersheds across the U.S., they still reflect the results of a targeted sample, not a full survey of all watersheds. Data are also highly aggregated and should only be interpreted as an indication of national patterns. 2. This indicator does not report the extent to which pesticide concentrations

may be above or below standards for human health; it just reports whether the standard has been exceeded. It also does not report the extent to which concentrations may exceed other reference values that were not used for this report (e.g., Maximum Contaminant Level Goals (MCLGs) for drinking water). 3. Many chemicals lack an established reference value for human health. Of the 80 pesticide-related chemicals screened, only 45 had drinking water standards or guidelines at the time the indicator was constructed. Current standards and guidelines also do not account for mixtures of pesticide chemicals and seasonal pulses of high concentrations. Possible pesticide effects on reproductive, nervous, and immune systems, as well as chemically sensitive individuals, are not yet well understood. 4. Contaminant levels do not necessarily reflect the concentrations that humans will be exposed to in their drinking water supply, as nitrate and pesticides may be partially or completely removed through water treatment. 5. Although limited historical data are available to characterize long-term trends in groundwater contamination, this indicator specifically examines just the most current conditions.